



The synergism between electro-Fenton and electrocoagulation process to remove Cu-EDTA

Wei Guan^{a,b}, Baofeng Zhang^a, Shichao Tian^c, Xu Zhao^{a,d,*}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, China

^c Environmental Science and Technology Laboratory, Tsinghua-Berkeley Shenzhen Institute, Shenzhen 518055, China

^d University of Chinese Academy of Sciences, No.19 (A) Yuquan Road, Shijingshan District, Beijing, 100049, China

ARTICLE INFO

Keywords:

Cu-EDTA

Electro-Fenton

Electrocoagulation

Hydroxyl radical

ABSTRACT

Heavy metal contamination in water has a serious risk to public health and other life forms on earth. In this study, the electrochemical destruction of Cu-EDTA and the removal of liberated Cu²⁺ ions with iron plate anode and stainless steel cathode were investigated. Cu-EDTA contaminant was destroyed by the combination of electro-Fenton and electrocoagulation method. Its performance was evaluated in terms of the destruction of Cu-EDTA as a function of the current density, H₂O₂ concentration and initial pH. When the current density was 72.92 A/m², the H₂O₂ concentration was 49.4 mM and the initial pH was 3.0, it was highly efficient for destruction of Cu-EDTA complexes and removal of copper ions from wastewater. The deposition generated in the electro-Fenton process was analyzed by Raman spectroscopy. The generated hydroxyl radicals in the electro-Fenton process were identified by the electron spin resonance, which was responsible for the destruction of Cu-EDTA.

1. Introduction

Heavy metals pollution in water has drawn increasing attentions because of their potential risks to human health and ecosystem [1,2]. The ethylenediaminetetraacetic acid (EDTA) as an organic complexing agent is widely used in electroplating, metallurgy and other industries to stabilize heavy metal ions [3,4]. If wastewater containing both copper and EDTA ions is not treated with suitable methods, it may cause significant environmental problems by forming stable Cu-EDTA complexes, resulting in an increased mobility of toxic metals to ground water, surface water and soil systems [5,6]. The completely natural degradation time of Cu-EDTA in soil is longer than 15 years [7]. Therefore, the contaminant should be removed before being discharged into the natural environments.

Currently, the most common treatment methods for heavy metal containing wastewater are chemical precipitation and biological treatment [8,9]. However, due to the high complexation affinity and high stability of Cu-EDTA over a wide pH range, it usually cannot be efficiently removed by these methods [10]. TiO₂-mediated photocatalytic treatment has been suggested as a promising technique, but the adsorption is identified as one of the important parameters in controlling the kinetics of Cu-EDTA oxidation [11]. In addition, the capacity of

photocatalytic oxidation is limited by some environmental conditions.

Electrocoagulation is an efficient method to treat heavy metal in wastewater from electroplating industry or smelting industry. During the electrocoagulation process, the pollutant can be removed by adsorption, sedimentation, electrostatic attraction, anodic oxidation and cathodic reduction [12]. The previous study has shown that copper ions could be easily removed in Cu-EDTA solution but EDTA ions were hard to be degraded due to its high stability [13]. Therefore, it is urgent to find a way to remove copper ions and EDTA simultaneously.

The combined technologies between electrocoagulation and other processing technology have been studied, such as electrocoagulation-membrane filtration and electrocoagulation-photolytic oxidation [14,15]. However, these methods are difficult to be applied due to the high cost and complicated process. Advanced oxidation processes have been proved to be effective for the rapid degradation of recalcitrant and non-biodegradable contaminants in wastewater [16]. Electrochemical advanced oxidation processes have received more attention over the last decade as an effective and suitable method for treating wastewater contaminated with toxic and persistent organic pollutants. The hydroxyl radicals ($\cdot\text{OH}$) have a high oxidation potential of 2.8 V (vs. NHE), which are non-selective reactive oxygen species for rapid degradation of organic contaminants. Therefore, electro-Fenton process is

* Corresponding author. P O Box 2871, 18 Shuangqing Road, Haidian District, Beijing, 10085, China.
E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

an effective method to remove organic pollutants in the wastewater. Compared with the traditional Fenton method, electro-Fenton process has the advantages such as high utilization efficiency of H_2O_2 and Fe^{2+} , cleaner process, less excess sludge and lower investment cost [17].

In this experiment, Cu-EDTA contaminant was destroyed by the combination of electro-Fenton and electrocoagulation. Then the generated copper ions and EDTA ions were removed by various processes including oxidation, reduction, adsorption, coagulation and co-precipitation. Effects of current density, H_2O_2 concentration and pH value on the removal efficiency of Cu-EDTA and TOC were investigated. The deposition generated in the electro-Fenton process was analyzed by the Raman spectroscopy. The generation of hydroxyl radicals in the system was confirmed by the electron spin resonance (ESR) technique.

2. Experiments

2.1. Chemicals

Copper sulfate (CuSO_4), sodium sulfate (Na_2SO_4), sodium perchlorate (NaClO_4), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical Reagent Co., Ltd. China. The reagent of 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma Chemical Reagent Co., Ltd. and stored at -20°C . All the chemicals were analytical grade and used without further purification. The solutions were prepared with Milli-Q water (Millipore, $18.2\text{ M}\Omega\text{ cm}$).

2.2. Experimental section

The experiments were performed in a glass reactor and the Cu-EDTA solutions were kept homogenous by a magnetic stirring apparatus. The initial concentration of Cu-EDTA was 1.0 mM and Na_2SO_4 acted as an electrolyte (0.05 M). The electrochemical reactor was shown in Fig. 1, it included a direct-current (DC) power supply, an electrolytic cell, a stainless steel plate, an iron plate and a magnetic stirring apparatus. The iron plate was used as anode and stainless steel plate was used as cathode, which were purchased from Beijing Henglitai Corporation. The electrochemical experiments were performed at the constant current mode controlled by a DC power (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). Cu-EDTA solution was prepared by adding CuSO_4 powder to Na_2EDTA solution at a molar ratio of $\text{Cu}^{2+}:\text{EDTA} = 1.0:1.0$ [18]. The pH value was adjusted by H_2SO_4 (0.2 M) or NaOH (0.2 M).

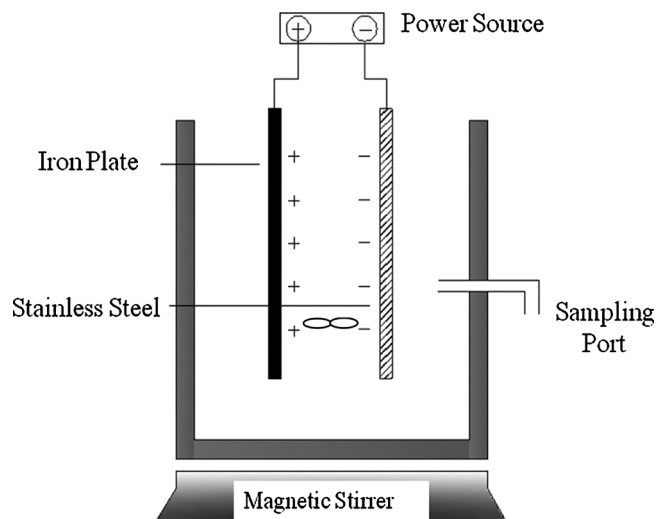


Fig. 1. Schematic diagram of the electrochemical reactor.

2.3. Analytical procedures

The concentration of Cu-EDTA was measured by a high-performance liquid chromatography (HPLC, 1260, Agilent Technology) with a C18 column and ultraviolet detector. The elution was comprised of 92% oxalic acid (concentration, 15 mM ; pH, 3.0)/8% acetonitrile (v/v) at a temperature of 25°C . The flow rate was set as 1 mL/min and the detection wavelength was set as 254 nm [19]. The concentrations of total copper ions and iron ions were measured using 700 series inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent Technology). Total organic carbon (TOC) was measured using a Shimadzu TOC analyzer (TOC-VCPH, Shimadzu, Japan) [20]. The pH value was measured using a 9165 BN pH electrode connected to an Orion-828 pH analyzer (Orion Research, Inc., Beverly, MA). The hydroxyl radicals were identified by the ESR on a Bruker ESR 300E with a microwave bridge (receiver gain, 1×10^5 ; modulation amplitude, 2 G ; microwave power, 10 mW ; modulation frequency, 100 kHz). The capture agent was dimethyl pyridine N-oxide (DMPO) [21]. In addition, *in situ* Raman spectroscopic studies were performed with a confocal Raman microscope (LabRAM HR 800, Horiba) equipped with an Ar laser (514 nm) and a $40\times$ objective.

3. Results and discussion

3.1. Hydrolysis form of Cu-EDTA and Fe-EDTA in different pH

The chemical property and form of Cu-EDTA were analyzed according to the hydrolysis function. It could be inferred that during the electro-Fenton and electrocoagulation process, the generation of iron ions reacted with Cu-EDTA, which would accelerate the removal efficiency of copper ions. The hydrolysis forms of Cu-EDTA complex in different pH were shown in Fig. 2 (a), when the pH was 3.0, the ions of copper and EDTA existed in CuHEDTA^- , Cu-EDTA^{2-} and CuH_2EDTA forms. When the pH was increased from 5.0 to 10.0, Cu-EDTA^{2-} became the main complex form and the complex constant of Cu-EDTA was high ($\lg K = 18.8$). Cu^{2+} (t) was the total concentration of free copper ions, including Cu^{2+} , Cu(OH)_2 (aq), Cu(OH)_3^- , $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_2(\text{OH})_3^+$, $\text{Cu}_3(\text{OH})_4^{2+}$ and Cu(OH)^+ . EDTA (t) was the total concentration of EDTA, including EDTA^{4-} , HEDTA^{3-} , $\text{H}_2\text{EDTA}^{2-}$, H_3EDTA^- , H_4EDTA (aq), H_5EDTA^+ and $\text{H}_6\text{EDTA}^{2+}$. The concentration of Cu-EDTA complex included Cu-EDTA^{2-} , CuH_2EDTA (aq), CuHEDTA^- and Cu(OH)EDTA^{3-} [22].

As shown in Fig. 2 (b), the substitution reaction would be influenced by pH value. When the pH was low, the concentration of free Fe^{3+} ions was low and the main form was Fe-EDTA. With the pH increasing, the concentration of Fe-EDTA was decreased and the concentration of Cu-EDTA was increased. The complex constant of Fe-EDTA ($\lg K$ (Fe-EDTA) = 25.1) was higher than Cu-EDTA ($\lg K$ (Cu-EDTA) = 18.8) [23], therefore, the copper ions could be easily substituted by iron ions.

3.2. Effect of current density on the removal efficiency of Cu-EDTA

The effect of current density on the removal efficiency of Cu-EDTA was investigated. As shown in Fig. 3, the removal efficiency of Cu-EDTA was increased with the current density increasing from 0 to 72.92 A/m^2 . When the current density was higher than 72.92 A/m^2 , the removal efficiency of Cu-EDTA would be decreased. The cell potentials were 1.6 V, 3.1 V, 4.2 V and 4.6 V for the applied current density of 10.42 A/m^2 , 31.25 A/m^2 , 72.92 A/m^2 and 114.58 A/m^2 , respectively. The results indicated that the increasing current density was beneficial to the destruction of Cu-EDTA. Fe^{2+} ions were released from iron anode with the application of an electric field through Eq. (1) and the generated Fe^{2+} ions reacted with H_2O_2 to produce $\cdot\text{OH}$ through Eq. (2) [24].



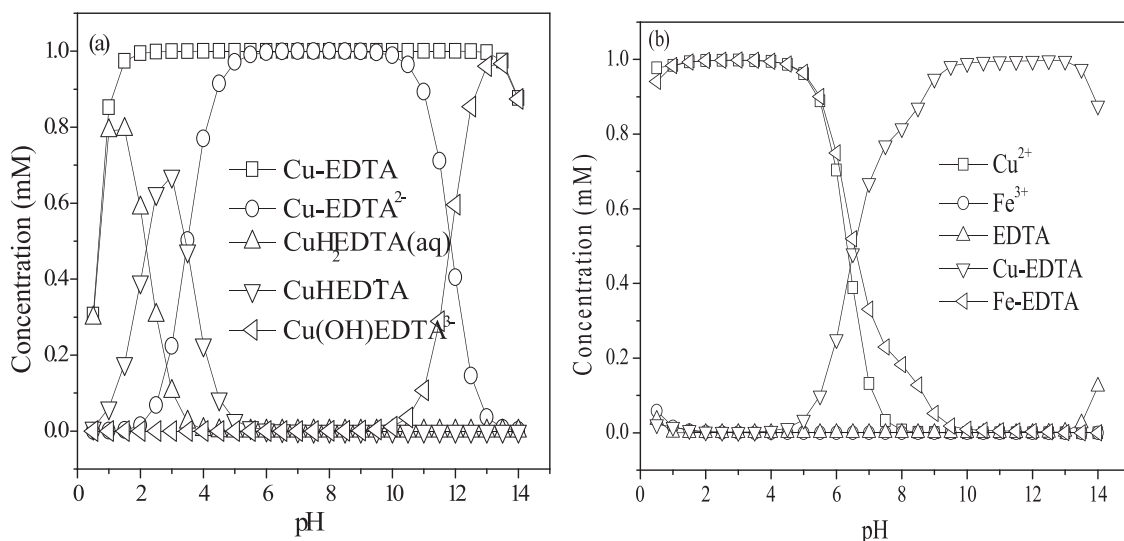


Fig. 2. The distribution of complex hydrolysis in different pH: (a) Cu-EDTA complex; and (b) Fe-EDTA complex ([Cu-EDTA] = 1.0 mM; [Fe-EDTA] = 1.0 mM; [Cu²⁺] = 1.0 mM).

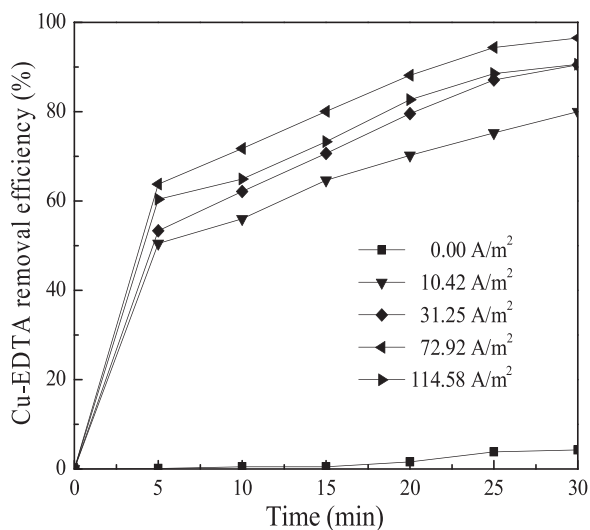


Fig. 3. Effect of current density on the removal efficiency of Cu-EDTA ([NaClO₄] = 10.0 mM; initial pH = 3.0; [Cu-EDTA] = 1.0 mM; [H₂O₂] = 24.7 mM).



The concentration of $\cdot\text{OH}$ was proportional to the concentration of iron ions and H_2O_2 in the electro-Fenton process, as shown in Eq. (3). Where k_1 is the second-order rate constant, λ is the average life of the $\cdot\text{OH}$, $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ are the concentrations of ferrous ion and hydrogen peroxide, respectively. When the current density was low, the main controlling factor was the concentration of Fe^{2+} ions during the electro-Fenton process, which would influence the generation of $\cdot\text{OH}$.

$$[\cdot\text{OH}] = \lambda \left(\frac{d[\cdot\text{OH}]}{dt} \right) = \lambda k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] \quad (3)$$

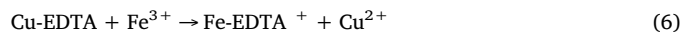
At high current density, the concentration of $\cdot\text{OH}$ was decreased due to the side-reactions. The further increase in current density could not provide any significant improvement in the removal efficiency of Cu-EDTA. This result could be explained by an enhanced rate of the side reactions which competed with the oxidative degradation of Cu-EDTA. The most important side reactions were: (i) evolution of H_2 (Eq. (4)) at the cathode which competed with the reduction of Cu^{2+} and (ii) evolution of O_2 (Eq. (5)) at the anode which competed with the production of $\cdot\text{OH}$ [25].



Furthermore, it was reported that the thickness of the diffusion layer would be decreased due to vigorous stirring of the solution by the generated gas, which would decrease the mass transfer coefficient [26]. Therefore, the removal efficiency of Cu-EDTA was decreased at current density of 114.58 A/m².

The existence form of residual EDTA included $\text{H}_n\text{EDTA}_{n-4}$, ($n \leq 4$), Fe-EDTA and Cu-EDTA after electro-Fenton oxidation. As shown in Fig. S1, most Cu (II) was substituted by Fe (III) to form Cu^{2+} ions and Fe-EDTA during the electrocoagulation process, but the total concentration of EDTA was unchanged. When H_2O_2 was added into the solution, EDTA was oxidized by the generation of $\cdot\text{OH}$ in the electro-Fenton process. Therefore, the removal of EDTA by the electro-Fenton method was easier than the electrocoagulation method.

During the electro-Fenton process for Cu-EDTA removal, the iron plate anode was electrolyzed and $\text{Fe}^{2+}/\text{Fe}^{3+}$ were generated under the electric field. As shown in Fig. S2 (a), the concentration of dissolved iron ions was rapidly increased at the initial 5 min, and then tended to stable. There were two kinds of iron ions in the solution, including highly soluble Fe^{2+} ions and the complexing Fe (III) [27]. The concentration of dissolved Cu^{2+} was decreased with the reaction time evolution and the concentration of dissolved Cu^{2+} was influenced by the current density (Fig. S2 (b)). The result indicated that Cu^{2+} was substituted by iron ions during the electrocoagulation process through Eq. (6) and the Cu^{2+} ions were reduced onto the cathode through Eq. (7) [28]:



3.3. Effect of H_2O_2 concentration on removal efficiency of Cu-EDTA

The effect of initial H_2O_2 concentration ranging from 0 to 98.8 mM was investigated in the electrochemical oxidation of Cu-EDTA. As shown in Fig. 4 (a), the removal efficiency of Cu-EDTA was increased significantly with increasing H_2O_2 concentration. When the concentration of H_2O_2 was increased from 0 to 49.4 mM, the removal efficiency of Cu-EDTA was increased markedly from 15.9% to 98.2% at 30 min. However, when the H_2O_2 concentration was increased from 49.4 mM to 98.8 mM, the removal efficiency of Cu-EDTA remained nearly unchanged. When the concentration of added H_2O_2 was low (4.94 mM), the removal efficiency of Cu-EDTA by electro-Fenton was

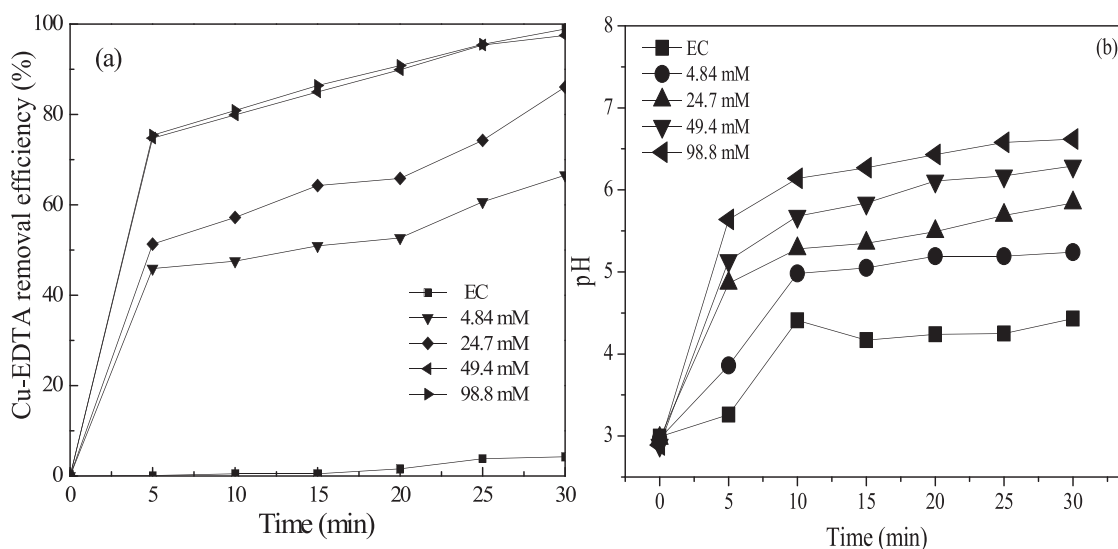


Fig. 4. (a) Effect of H₂O₂ concentration on the removal efficiency of Cu-EDTA; and (b) effect of H₂O₂ concentration on pH value during Cu-EDTA removal ([NaClO₄] = 10.0 mM; initial pH = 3.0; current density = 72.92 A/m²; [Cu-EDTA] = 1.0 mM).

66.7%. This was because the concentration of $\cdot\text{OH}$ produced during the electro-Fenton process was too low to completely mineralize EDTA. With the concentration of added H₂O₂ increasing, the concentration of $\cdot\text{OH}$ generated in the electro-Fenton process was higher and the removal efficiency of Cu-EDTA was increased. Taking the economy and performance into consideration, the optimal H₂O₂ concentration for Cu-EDTA removal was 49.4 mM. According to Fig. 4 (b), the pH value was increased with the H₂O₂ concentration increasing. During the electro-Fenton process, more OH[−] ions were generated through Eq. (2) [29].

Raman spectroscopy was a nondestructive technique to determine the quality of crystalline or amorphous materials, including surface conditions and homogeneity [30]. The Raman spectrum of deposition was shown in Fig. 5, which contained five bands at about 222, 288, 398, 490 and 605 cm^{−1}. These peaks could be assigned to the 2A₁g and 3E_g Raman modes for the typical hematite phase, which indicated that the deposition was $\alpha\text{-Fe}_2\text{O}_3$ [31,32]. During the process, Fe²⁺ ions were transformed to Fe³⁺ ions, and then reacted with OH[−] to form $\alpha\text{-Fe}_2\text{O}_3$.

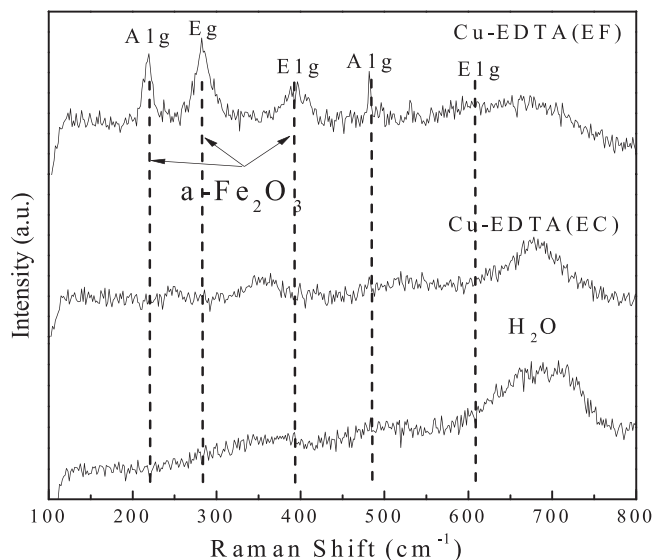


Fig. 5. The analysis of Raman spectrum for the generated flocs ([NaClO₄] = 10.0 mM; initial pH = 3.0; current density = 72.92 A/m²; [Cu-EDTA] = 1.0 mM; [H₂O₂] = 49.4 mM).

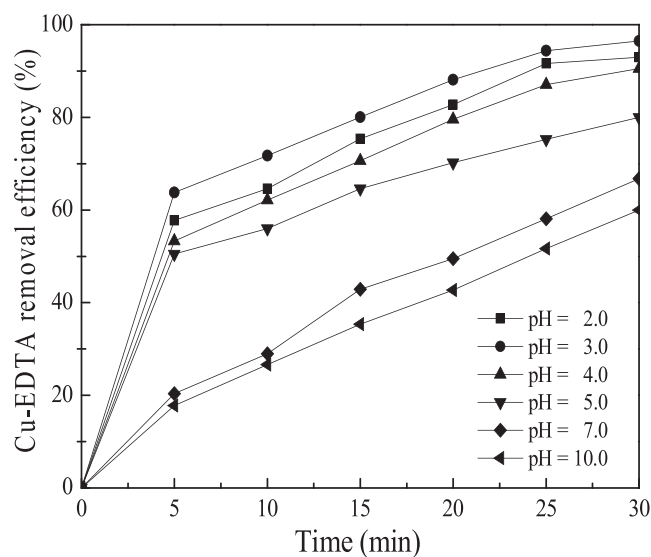
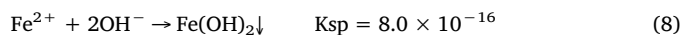


Fig. 6. Effect of initial pH on removal efficiency of Cu-EDTA ([NaClO₄] = 10.0 mM; current density = 72.92 A/m²; [Cu-EDTA] = 1.0 mM; [H₂O₂] = 49.4 mM).

3.4. Effect of pH value on removal efficiency of Cu-EDTA

The pH value generally has a significant effect on the electro-Fenton process. The removal efficiency of Cu-EDTA was influenced by pH value during the electro-Fenton process. As shown in Fig. 6, the removal efficiency of Cu-EDTA was the highest when the pH was 3.0. With the pH value increasing, the removal efficiency of Cu-EDTA was decreased. A high concentration of H⁺ (a low pH value) could lead to the side reaction of H₂ evolution, which inevitably took up at least some active sites for Cu²⁺ ions reduction. At the same time, according to Eq. (8), the pH value should be less than 6.6 in order to avoid the formation of Fe(OH)₂ precipitation in the solution.



In the meanwhile, at low pH value, Fe(OH)⁺ can be formed, which would compete with Fe²⁺ to react with H₂O₂. However, Fe(OH)⁺ reacted with H₂O₂ more slowly and would lead to less generation of hydroxyl radicals. Moreover, at very low pH value, hydroxyl radicals would be scavenged by H⁺ and the reaction between Fe²⁺ and H₂O₂

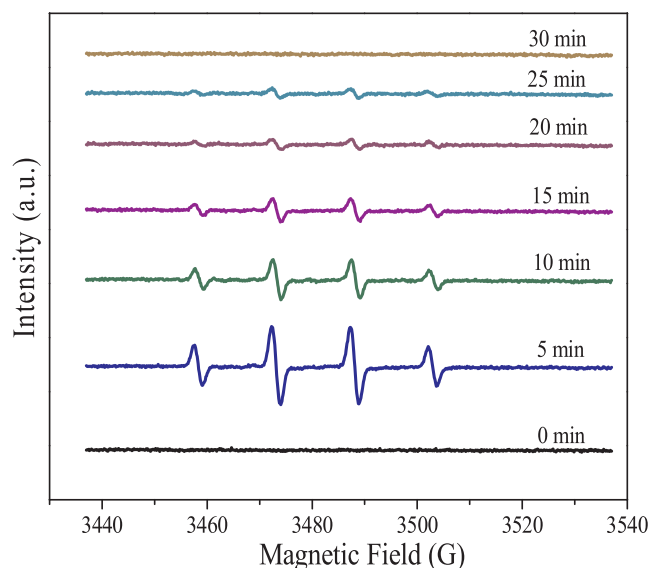


Fig. 7. The variation of hydroxyl radicals concentration during the electro-Fenton process ([NaClO_4] = 10.0 mM; current density = 72.92 A/m^2 ; [Cu-EDTA] = 1.0 mM; [H_2O_2] = 49.4 mM; initial pH = 3.0).

was inhibited [33]. As shown in Fig. S3, the trend of TOC removal was similar to Cu-EDTA removal at different pH value. Therefore, the pH value should be increased and the optimal pH value for the electro-Fenton process to remove Cu-EDTA contaminant was 3.0.

3.5. Analysis of hydroxyl radicals

Hydroxyl radicals were generally generated as oxidant species in the electro-Fenton process. At acid condition, the reaction between ferrous ions and hydrogen peroxide could lead to the generation of $\cdot\text{OH}$ radicals. DMPO spin-trap was used to detect the reactive oxygen species (ROS) involved in electro-Fenton process [34]. The variation of ESR signal intensity at different reaction time was shown in Fig. 7, the measured ESR spectra exhibited the characteristic 4-fold peak of DMPO- $\cdot\text{OH}$ adducts with an intensity ratio of 1:2:2:1 [35,36]. Moreover, no radical signal was detected at the beginning of experiment and the intensity of the peak was increased at the initial 5 min. However, the intensity of the peak was decreased after 5 min reaction. The concentration of $\cdot\text{OH}$ was proportional to the concentrations of iron ions and H_2O_2 in the electro-Fenton process. During the electro-Fenton process, the concentration of H_2O_2 would be decreased and the generated $\cdot\text{OH}$ would be consumed by the targeted contaminants. Therefore, the intensity of the peak was decreased after 5 min reaction.

4. Conclusions

In this experiment, a synergism between electro-Fenton and electrocoagulation was used to destroy Cu-EDTA complexes in wastewater, which simultaneously achieved the oxidation of EDTA and the removal of copper metal. The hydrolysis form of Cu-EDTA was influenced by pH. When the pH was 3.0, [Cu] and [EDTA] were existed in the form of CuHEDTA^- , Cu-EDTA^{2-} and CuH_2EDTA . When the pH ranged from 5.0 to 10.0, Cu-EDTA^{2-} was the main complex form, which was easy to be substituted by Fe^{3+} ions. In addition, effects of current density, H_2O_2 concentration and initial pH value on Cu-EDTA removal were analyzed. When the current density was 72.92 A/m^2 , the H_2O_2 concentration was 49.4 mM and the initial pH was 3.0, it was highly efficient for destruction of Cu-EDTA complexes and removal of copper ions from wastewater. The liberated copper ions were efficiently removed by various processes including adsorption, coagulation, co-precipitation and cathodic reduction. Hydroxyl radicals were responsible for the

destruction of Cu-EDTA and the generation of hydroxyl radicals was confirmed by ESR analysis. The deposition generated in this system was analyzed by the Raman spectroscopy and was confirmed to be $\alpha\text{-Fe}_2\text{O}_3$.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 51608086, 21377148); The Science and Technology Project from Chongqing (cstc2015jcyjA20027); Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ1501103); The Natural Science Foundation of Yongchuan, Chongqing (Ycstc, 2014ac4001).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.036>.

References

- [1] Z. Xu, C. Shan, B.H. Xie, Y. Liu, B.C. Pan, Decomplexation of Cu(II)-EDTA by UV/persulfate and UV/ H_2O_2 : efficiency and mechanism, *Appl. Catal. B Environ.* 200 (2017) 439–447.
- [2] M. Hua, S.J. Zhang, B.C. Pan, W.M. Zhang, L. Lv, Q.X. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: a review, *J. Hazard. Mater.* 211–212 (2012) 317–331.
- [3] K.A. Sashkina, A.V. Polukhin, V.S. Labko, A.B. Ayupov, A.I. Lysikov, E.V. Parkhomchuk, Fe-silicalites as heterogeneous Fenton-type catalysts for radio-cobalt removal from EDTA chelates, *Appl. Catal. B Environ.* 185 (2016) 353–361.
- [4] X.F. Huang, B.H. Xie, X.C. Li, B.C. Pan, S.J. Yuan, Y.Y. Zhang, C. Shan, Enhanced $\text{HO}\cdot$ production from ozonation activated by EDTA, *Chem. Eng. J.* 288 (2016) 562–568.
- [5] P.X. Wu, J.B. Zhou, X.R. Wang, Y.P. Dai, Z. Dang, N.W. Zhu, P. Li, J.H. Wu, Adsorption of Cu-EDTA complexes from aqueous solutions by polymeric Fe/Zr pillared montmorillonite: behaviors and mechanisms, *Desalination* 277 (2011) 288–295.
- [6] G.X. Yang, H. Jiang, Amino modification of biochar for enhanced adsorption of copper ions from synthetic wastewater, *Water Res.* 48 (2014) 396–405.
- [7] Z.L. Zou, R.L. Qiu, W.H. Zhang, H.Y. Dong, Z.H. Zhao, T. Zhang, X.G. Wei, X.D. Cai, The study of operating variables in soil washing with EDTA, *Environ. Pollut.* 157 (2009) 229–236.
- [8] C.K. Mbamba, D.J. Batstone, X. Flores-Alsina, S. Tait, A generalised chemical precipitation modelling approach in wastewater treatment applied to calcite, *Water Res.* 68 (2015) 342–353.
- [9] M. GopiKiran, K. Pakshirajan, G. Das, An overview of sulfidogenic biological reactors for the simultaneous treatment of sulfate and heavy metal rich wastewater, *Chem. Eng. Sci.* 158 (2017) 606–620.
- [10] F. Liu, C. Shan, X.L. Zhang, Y.Y. Zhang, W.M. Zhang, B.C. Pan, Enhanced removal of EDTA-chelated Cu(II) by polymeric anion-exchanger supported nanoscale zero-valent iron, *J. Hazard. Mater.* 321 (2017) 290–298.
- [11] X. Zhao, L.B. Guo, C.Z. Hu, H.J. Liu, J.H. Qu, Simultaneous destruction of Nickel (II)-EDTA with TiO_2/Ti film anode and electrodeposition of nickel ions on the cathode, *Appl. Catal. B Environ.* 144 (2014) 478–485.
- [12] A. Thiam, M.H. Zhou, E. Brillas, I. Sirés, Two-step mineralization of tartrazine solutions: study of parameters and by-products during the coupling of electrocoagulation with electrochemical advanced oxidation processes, *Appl. Catal. B: Environ.* 150–151 (2014) 116–125.
- [13] M. Pocięcha, D. Lestan, Using electrocoagulation for metal and chelant separation from washing solution after EDTA leaching of Pb, Zn and Cd contaminated soil, *J. Hazard. Mater.* 174 (2010) 670–678.
- [14] C. Durante, M. Cuscov, A.A. Isse, G. Sandoñà, A. Gennaro, Advanced oxidation processes coupled with electrocoagulation for the exhaustive abatement of Cr-EDTA, *Water Res.* 45 (2011) 2122–2130.
- [15] M. Boroski, A.C. Rodrigues, J.C. Garcia, L.C. Sampaio, J. Nozaki, N. Hioka, Combined electrocoagulation and TiO_2 photoassisted treatment applied to wastewater effluents from pharmaceutical and cosmetic industries, *J. Hazard. Mater.* 162 (2009) 448–454.
- [16] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. a review, *Crit. Rev. Env. Sci. Tec.* 44 (2014) 2577–2641.
- [17] F. Sopaj, N. Oturan, J. Pinson, F. Podvorica, M.A. Oturan, Effect of the anode materials on the efficiency of the electro-Fenton process for the mineralization of the antibiotic sulfamethazine, *Appl. Catal. B Environ.* 199 (2016) 331–341.
- [18] S.Y. Lan, Y. Xiong, S.H. Tian, J.X. Feng, T.Y. Xie, Enhanced self-catalytic degradation of CuEDTA in the presence of $\text{H}_2\text{O}_2/\text{UV}$: Evidence and importance of Cuperoxide as a photo-active intermediate, *Appl. Catal. B Environ.* 183 (2016) 371–376.
- [19] H.B. Zeng, S.C. Tian, H.F. Liu, B.Y. Chai, X. Zhao, Photo-assisted electrolytic decomplexation of Cu-EDTA and Cu recovery enhanced by H_2O_2 and electro-generated active chlorine, *Chem. Eng. J.* 301 (2016) 371–379.

- [20] M. Zhang, W.J. Luo, Z. Wei, W.J. Jiang, D. Liu, Y.F. Zhu, Separation free C_3N_4/SiO_2 hybrid hydrogels as high active photocatalysts for TOC removal, *Appl. Catal. B Environ.* 194 (2016) 105–110.
- [21] S.C. Tian, Y.B. Li, X. Zhao, Cyanide removal with a copper/active carbon fiber cathode via a combined oxidation of a Fenton-like reaction and in situ generated copper oxides at anode, *Electrochim. Acta* 180 (2015) 746–755.
- [22] X. Zhao, L.B. Guo, J.H. Qu, Photoelectrocatalytic oxidation of Cu-EDTA complex and electrodeposition recovery of Cu in a continuous tubular photoelectrochemical reactor, *Chem. Eng. J.* 239 (2014) 53–59.
- [23] W. Sunda, S.S. Huntsman, Effect of pH, light, and temperature on Fe-EDTA chelation and Fe hydrolysis in seawater, *Mar. Chem.* 84 (2003) 35–47.
- [24] N. Barhoumi, N. Oturan, H. Olvera-Vargas, E. Brillas, A. Gadri, S. Ammar, M.A. Oturan, Pyrite as a sustainable catalyst in electro-Fenton process for improving oxidation of sulfamethazine. Kinetics, mechanism and toxicity assessment, *Water Res.* 94 (2016) 52–61.
- [25] N. Oturan, J. Wu, H. Zhang, V.K. Sharma, M.A. Oturan, Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: effect of electrode materials, *Appl. Catal. B-Environ.* 140 (2013) 92–97.
- [26] X.S. Cai, J.L. Zheng, J. Wärnå, T. Salmi, B. Taouk, S. Leveneur, Influence of gas-liquid mass transfer on kinetic modeling: carbonation of epoxidized vegetable oils, *Chem. Eng. J.* 313 (2017) 1168–1183.
- [27] D. Kolodyński, H. Hubicka, Z. Hubicki, Sorption of heavy metal ions from aqueous solutions in the presence of EDTA on monodisperse anion exchangers, *Desalination* 227 (2008) 150–166.
- [28] L. Liu, R.Z. Li, Y. Liu, J.D. Zhang, Simultaneous degradation of ofloxacin and recovery of Cu (II) by photoelectrocatalysis with highly ordered TiO_2 nanotubes, *J. Hazard. Mater.* 308 (2016) 264–275.
- [29] H. Zazou, N. Oturan, M. Sönmez-Çelebi, M. Hamdani, M.A. Oturan, Mineralization of chlorobenzene in aqueous medium by anodic oxidation and electro-Fenton processes using Pt or BDD anode and carbon felt cathode, *J. Electroanal. Chem.* 774 (2016) 22–30.
- [30] X.L. Hu, J.C. Yu, J.M. Gong, Fast production of self-assembled hierarchical r- Fe_2O_3 nanoarchitectures, *J. Phys. Chem. C* 111 (2007) 11180–11185.
- [31] Z.M. Zhang, C.T. Gao, Y.X. Li, W.H. Han, W.B. Fu, Y.M. He, E.Q. Xie, Enhanced charge separation and transfer through Fe_2O_3/ITO nanowire arrays wrapped with reduced graphene oxide for water-splitting, *Nano Energy* 30 (2016) 892–899.
- [32] Y.L. Nie, C. Hu, N.N. Li, L. Yang, J.H. Qu, Inhibition of bromate formation by surface reduction in catalytic ozonation of organic pollutants over β - $FeOOH/Al_2O_3$, *Appl. Catal. B Environ.* 147 (2014) 287–292.
- [33] X.X. Liu, S.H. Yuan, M. Tong, D. Liu, Oxidation of trichloroethylene by the hydroxyl radicals produced from oxygenation of reduced nontonite, *Water Res.* 113 (2017) 72–79.
- [34] H.C. Lan, J.F. Li, M. Sun, X.Q. An, C.Z. Hu, R.P. Liu, H.J. Liu, J.H. Qu, Efficient conversion of dimethylarsinate into arsenic and its simultaneous adsorption removal over FeC_x/N -doped carbon fiber composite in an electro-Fenton process, *Water Res.* 100 (2016) 57–64.
- [35] S.C. Tian, Y.B. Li, H.B. Zeng, W. Guan, Y. Wang, X. Zhao, Cyanide oxidation by singlet oxygen generated via reaction between H_2O_2 from cathodic reduction and OCl^- from anodic oxidation, *J. Colloid Interface Sci.* 482 (2016) 205–211.
- [36] M. Manciu, F.S. Manciu, E. Ruckenstein, On the surface tension and Zeta potential of electrolyte solutions, *Adv. Colloid Interface Sci.* 244 (2016) 90–99.